Free power dissipation from functional line integration

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Power functional theory provides an exact generalisation of equilibrium density functional theory to non-equilibrium systems undergoing Brownian many-body dynamics. Practical implementation of this variational approach demands knowledge of an excess (over ideal gas) dissipation functional. Using functional line integration (i.e. the operation inverse to functional differentiation), we obtain an exact expression for the excess free power dissipation, which involves the pair interaction potential and the two-body, equal-time density correlator. This provides a basis for the development of approximation schemes.

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1. Introduction

Classical density functional theory (DFT) provides an exact variational framework for addressing the thermodynamics and static microstructure of inhomogeneous fluids in equilibrium [1–3]. Within DFT, the non-trivial many-body physics due to the interparticle interactions follows from the intrinsic excess Helmholtz free-energy functional. The functional is intrinsic in the sense that it is independent of external potential energy fields and hence depends solely on the interparticle interaction potential. However, the excess free energy is only known exactly in a few limiting cases and for special models, such as the low-density functional virial expansion and one-dimensional hard-rod model [4]. Approximations are hence unavoidable for any realistic model fluid. Even though the DFT formalism was essentially complete by the late 1970s, the development of approximate 'fundamental measures' [5] excess free-energy functionals, capable of accurately describing realistic three-dimensional models, required several decades of intense research.

Power functional theory (PFT) has recently been proposed as an exact generalisation of DFT for Brownian dynamics of many-body systems out-of-equilibrium [6]. The framework consolidates DFT (which follows when imposing an equilibrium condition on the power functional) and dynamical density functional theory (DDFT) as special cases into a unified variational scheme. Furthermore, PFT facilitated the development of a non-equilibrium Ornstein–Zernike equation [7,8] for time-dependent two-body correlation functions. This has opened up new possibilities for the description of structural relaxation in dense systems and presents intriguing connections with mode-coupling theory.

Within PFT, the interparticle interactions are solely contained in the intrinsic excess (over ideal gas) free power functional, which is a dynamical analogue of the excess Helmholtz free energy in equilibrium. However, in contrast to the equilibrium case, our knowledge about the intrinsic excess free power is presently very limited. Although some (physically motivated) forms for this functional have been suggested [6], explicit expressions for this central object have so far been lacking.

In this paper, we employ methods of dynamical functional calculus in order to gain further insight into the excess intrinsic power functional. In the previous work [6], a physically intuitive splitting of this quantity into the sum of adiabatic and superadiabatic contributions was suggested, where the former is related to the equilibrium free energy and the latter remained unspecified. We here demonstrate how the splitting arises naturally from the application of functional line integration (which is the operation inverse to functional differentiation) and how this leads to a well-defined, statistical mechanical expression for the excess dissipation, given in terms of a two-point density correlator. These developments pave the way for systematic approximation schemes, which treat many-body colloidal dynamics at the superadiabatic level.

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The paper is structured as follows. In Section 2, we specify the method of functional line integration, which appears to be an under-used tool for formulating perturbative solutions to variational problems. In Section 3, we show how this method is applied in equilibrium to obtain exact sum rules connecting the free energy with spatial correlation functions. In Section 4, we generalise the methodology to non-equilibrium, working now within the framework of PFT. Our central result is a formally exact expression for the excess dissipation functional (Equations (43) and (44)). This provides a basis for the development of approximation schemes. Finally, in Section 5, we give some conclusions and provide an outlook for future work.

2. Functional line integration

In elementary calculus, integration is the operation inverse to differentiation: a derivative can be integrated up to recover the original function to within an integration constant. In the multidimensional case, the gradient of a function can be integrated along a line in the multidimensional space in order to recover, again up to a constant, the original function. (The relationship between a conservative force and its potential energy might serve as a prime physical example.) For singly connected integration domains, the integration line can be chosen arbitrarily.

Here we recall that in functional calculus, there is a similar inverse operation to functional differentiation, by which a functional can be reconstructed (up to an integration constant) from its derivative [9]. As there does not appear to be any standard terminology for this operation, we will henceforth refer to it as a 'functional line integral' (not to be confused with the Feynman– Wiener *path* integral [10]).

Consider the functional $H[g]$, where $g(\mathbf{r})$ is an arbitrary function of a spatial coordinate $\mathbf{r}$. If we already know the functional derivative

$$\frac{\delta H[g]}{\delta g(\mathbf{r})}, \tag{1}$$

then we can exploit this information to recover the original functional by integration. The operation which achieves this, the functional line integral, is given by

$$H[g] = H[g_r] + \int d\mathbf{r} \int_{g_r(\mathbf{r})}^{g(\mathbf{r})} d\tilde{g}(\mathbf{r}) \frac{\delta H[\tilde{g}]}{\delta \tilde{g}(\mathbf{r})}, \tag{2}$$

where $g_r(\mathbf{r})$ is a reference function. The notation $\tilde{g}(\mathbf{r})$ denotes a dummy integration variable and we use the following short-hand notation:

$$\frac{\delta H[\tilde{g}]}{\delta \tilde{g}(\mathbf{r})} \equiv \left.\frac{\delta H[g]}{\delta g(\mathbf{r})}\right|_{g(\mathbf{r})=\tilde{g}(\mathbf{r})}. \tag{3}$$

The integration in (2) is a standard one-dimensional integral over the value of $\tilde{g}$ at point $\mathbf{r}$, from its reference value, $g_r(\mathbf{r})$, to its target value, $g(\mathbf{r})$. The integral is taken along a path in function space and, provided that $H[g]$ is unique, the result will be path-independent.

Without loss of generality, we choose a linear parametric path through function space:

$$\tilde{g}(\mathbf{r}) \equiv g_\alpha(\mathbf{r}) = g_r(\mathbf{r}) + \alpha(g(\mathbf{r}) - g_r(\mathbf{r})), \tag{4}$$

where the 'charging parameter' α varies within the range $0 \leq \alpha \leq 1$. Equation (2) thus becomes

$$H[g] = H[g_r] + \int_0^1 d\alpha \int d\mathbf{r}\, \Delta g(\mathbf{r}) \frac{\delta H[g_\alpha]}{\delta g_\alpha(\mathbf{r})}, \tag{5}$$

where $\Delta g(\mathbf{r}) \equiv g(\mathbf{r}) - g_r(\mathbf{r})$. The α integration requires knowledge of the functional derivative for all values of α, from the reference ($\alpha = 0$) to the target ($\alpha = 1$) function.

The derivative of a vector-valued functional L with vectorial argument $\mathbf{v}(\mathbf{r})$ can be integrated according to

$$L[\mathbf{v}] = L[\mathbf{v}_r] + \int_0^1 d\alpha \int d\mathbf{r}\, \Delta\mathbf{v}(\mathbf{r}) \cdot \frac{\delta L[\mathbf{v}_\alpha]}{\delta \mathbf{v}_\alpha(\mathbf{r})}, \tag{6}$$

where $\Delta\mathbf{v}(\mathbf{r}) \equiv \mathbf{v}(\mathbf{r}) - \mathbf{v}_r(\mathbf{r})$ is the deviation from the reference function $\mathbf{v}_r(\mathbf{r})$ and the integrand is the scalar product of two vector quantities.

The generalisation of Equation(5) to functionals of functions with multiple arguments is straightforward. For example, the first derivative of the functional $G[f(\mathbf{r}, \mathbf{r}')]$ can be integrated to obtain

$$G[f] = G[f_r] + \int_0^1 d\alpha \int d\mathbf{r} \int d\mathbf{r}'\, \Delta f(\mathbf{r}, \mathbf{r}') \frac{\delta G[f_\alpha]}{\delta f_\alpha(\mathbf{r}, \mathbf{r}')}, \tag{7}$$

where $\Delta f(\mathbf{r}, \mathbf{r}') \equiv f(\mathbf{r}, \mathbf{r}') - f_r(\mathbf{r}, \mathbf{r}')$, and we have again assumed a linear integration path.

3. Equilibrium

As described very clearly by Evans [2], there are several routes to the equilibrium free energy of an inhomogeneous fluid via integration of appropriate correlation functions. The required mathematical tool for expressing such relations is functional line integration. In this section, we will review and extend (cf. Equation (19)) some equilibrium results, in order to provide context for our subsequent non-equilibrium considerations and to demonstrate how functional line integration is a powerful method for constructing approximations.

3.1. *Density functional theory*

The key object in classical DFT is the grand potential functional, given by [1,2]

$$\beta\Omega[\rho\,] = F^{\rm id}[\rho\,] + F^{\rm exc}[\rho\,] - \int d\mathbf{r}\,(\mu - V_{\rm ext}(\mathbf{r}))\,\rho(\mathbf{r}), \tag{8}$$

where μ and $V_{\rm ext}(\mathbf{r})$ are the chemical and external potentials, respectively. The first term in Equation (8) is the Helmholtz free energy of the ideal gas:

$$F^{\rm id}[\rho] = k_{\rm B}T \int d\mathbf{r}\,\rho(\mathbf{r})[\ln(\Lambda^3\rho(\mathbf{r},t)) - 1], \tag{9}$$

where $k_{\rm B}$ is Boltzmann's constant, T is the temperature and Λ is the thermal wavelength. $F^{\rm exc}[\rho\,]$ is the excess (over ideal) Helmholtz free energy, which is the only contribution that contains interparticle interactions. The grand potential satisfies the minimum condition

$$\frac{\delta\Omega[\rho\,]}{\delta\rho(\mathbf{r})} = 0, \tag{10}$$

at the physically realised equilibrium density distribution. Equation (10) thus generates a formally exact equation for the equilibrium one-body density.

3.2. *Integration of the direct correlation functions*

Repeated functional differentiation of the excess Helmholtz free energy with respect to the one-body density generates the hierarchy of direct correlation functions [1,2]. The first member of the hierarchy is the one-body direct correlation function, which is defined by

$$c^{(1)}(\mathbf{r}\,;[\rho\,]) = -\frac{\delta\beta F^{\rm exc}[\rho\,]}{\delta\rho(\mathbf{r})}, \tag{11}$$

where $\beta = (k_{\rm B}T)^{-1}$ and we make the functional dependence on the density explicit in the notation. Higher body direct correlation functions are defined by the recursion relation

$$c^{(n)}(\mathbf{r}_1,\ldots,\mathbf{r}_n\,;[\rho\,]) = \frac{\delta c^{(n-1)}(\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}\,;[\rho\,])}{\delta\rho(\mathbf{r}_n)}. \tag{12}$$

Functional line integration of the direct correlation functions yields the excess Helmholtz free energy. Choosing a linear path through the space of density functions,

$$\rho_\alpha(\mathbf{r}) = \rho_r(\mathbf{r}) + \alpha(\rho(\mathbf{r}) - \rho_r(\mathbf{r})), \tag{13}$$

and integrating Equation (11) yields a formal result for the excess free energy

$$\beta F^{\rm exc}[\rho\,] = \beta F^{\rm exc}[\rho_r\,] - \int_0^1 d\alpha \int d\mathbf{r}\Delta\rho(\mathbf{r})c^{(1)}(\mathbf{r};[\rho_\alpha]), \tag{14}$$

where $\Delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_r(\mathbf{r})$.

The integrand of Equation (14), which is a functional of the parameterised density $\rho_\alpha(\mathbf{r})$, can be obtained by integrating Equation (12), with $n = 2$, along a linear path,

$$c^{(1)}(\mathbf{r},[\rho_\alpha]) = c^{(1)}(\mathbf{r}\,;[\rho_r]) + \int_0^\alpha d\alpha' \int d\mathbf{r}'\Delta\rho(\mathbf{r}')c^{(2)}(\mathbf{r},\mathbf{r}';[\rho_{\alpha'}]). \tag{15}$$

In bulk, the one-body direct correlation function becomes spatially constant and Equation (15) is equivalent to the first of Baxter's sum rules [11]:

$$\frac{\partial c^{(1)}(\rho_b)}{\partial\rho_b} = \int d\mathbf{r}\,c^{(2)}(r\,;\rho_b), \tag{16}$$

where the two-body direct correlation function depends only on a single scalar argument.

Substitution of Equation (15) into Equation (14) yields the desired expression for the free-energy functional,

$$\beta F^{\rm exc}[\rho\,] = \beta F^{\rm exc}[\rho_r\,] - \int d\mathbf{r}\Delta\rho(\mathbf{r})c^{(1)}(\mathbf{r}\,;[\rho_r]) - \int_0^1 d\alpha(1-\alpha)\int d\mathbf{r} \times \int d\mathbf{r}'\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')c^{(2)}(\mathbf{r},\mathbf{r}';[\rho_\alpha]). \tag{17}$$

This is a formally exact result which provides a starting point for approximation schemes. For example, taking the reference density to be that of a bulk system, $\rho_r(\mathbf{r}) = \rho_b =$ const, and neglecting the α dependence of the integrand yields

$$\beta F^{\rm exc}_{\rm RY}[\rho\,] = \beta F^{\rm exc}[\rho_b] - \int d\mathbf{r}\Delta\rho(\mathbf{r})c^{(1)}(\rho_b) - \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')c^{(2)}(|\mathbf{r}-\mathbf{r}'|;\rho_b), \tag{18}$$

which is the well-known quadratic functional, first employed by Ramakrishnan and Youssouff (RY) in their study of crystallisation [12]. Equation (18) requires as input the bulk two-body direct correlation function, available for example, from integral equation theory [3].

Equation (18) is identical to a truncated functional Taylor expansion of the excess free energy. The remainder,

given by the sum of all terms of cubic and higher order, is known as the 'bridge functional' [13]. A closed-form expression for this quantity is found by integration of Equation (12), with $n = 3$, and substitution of the result into Equation (17). This yields

$$\beta F^{\mathrm{exc}}[\rho]=\beta F^{\mathrm{exc}}_{\mathrm{RY}}[\rho\,]-\frac{1}{2}\int_0^1 d\alpha(1-\alpha)^2\int d\mathbf{r}\int d\mathbf{r}'\int d\mathbf{r}'' \times \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')\Delta\rho(\mathbf{r}'')c^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'';[\rho_\alpha]), \quad (19)$$

where the second term is the bridge functional.

3.3. Integration of the pair density

A further exact expression for the excess free energy can be obtained by integrating the two-body density correlator [2]. Starting from the grand canonical partition function, it is straightforward to show that

$$\frac{\delta F^{\mathrm{exc}}[\rho\,]}{\delta\phi(\mathbf{r},\mathbf{r}')}=\frac{1}{2}\rho^{(2)}(\mathbf{r},\mathbf{r}'), \quad (20)$$

where $\phi(\mathbf{r},\ \mathbf{r}')$ is the interaction pair potential and $\rho^{(2)}(\mathbf{r},\mathbf{r}')$ is the two-body density [3]. (Note that Equation (20) remains valid if triplet and higher body interparticle interactions are present.) Functional line integration in the space of pair potentials yields

$$\beta F^{\mathrm{exc}}[\rho\,]=\beta F^{\mathrm{exc}}[\rho_r] +\frac{1}{2}\int_0^1 d\alpha\int d\mathbf{r}\int d\mathbf{r}'\Delta\phi(\mathbf{r},\mathbf{r}')\rho^{(2)}(\mathbf{r},\mathbf{r}';[\phi_\alpha]), \quad (21)$$

where the choice $\phi_\alpha(\mathbf{r},\mathbf{r}')=\phi_r(\mathbf{r},\mathbf{r}')+\alpha\Delta\phi(\mathbf{r},\mathbf{r}')$ enables a part of the interaction potential to be 'turned on' by increasing α. Here $\Delta\phi(\mathbf{r},\mathbf{r}')=\phi(\mathbf{r},\mathbf{r}')-\phi_r(\mathbf{r},\mathbf{r}')$ is the difference between the full pair potential and that of the reference system.

Equation (21) forms the basis of virtually all liquid state perturbation theories. Neglecting the dependence of the integrand on α yields a first-order theory [14]. Furthermore, if the two-body density of the reference system is factorised, $\rho^{(2)}(\mathbf{r},\mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')g^{(2)}(\mathbf{r},\mathbf{r}')\approx\rho(\mathbf{r})\rho(\mathbf{r}')$, such that the inhomogeneous pair correlation function $g^{(2)}(\mathbf{r},\mathbf{r}')\approx 1$, then we recover the familiar mean-field approximation [1,2]

$$\beta F^{\mathrm{exc}}[\rho]=\beta F^{\mathrm{exc}}[\rho_r]+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\Delta\phi(\mathbf{r},\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}'), \quad (22)$$

which is frequently employed to treat the attractive part of the interparticle attraction, $\Delta\phi(\mathbf{r},\mathbf{r}')\equiv\phi_{\mathrm{att}}(\mathbf{r},\mathbf{r}')$, as a perturbation to the hard-sphere reference system.

4. Non-equilibrium

The PFT [6] is the generalisation of DFT to treat non-equilibrium systems undergoing Brownian dynamics. Derivatives of the power functional with respect to external, density or current fields are related to *dynamic* correlation functions [7,8]. We will here focus on functional line integration with respect to the current.

4.1. Power functional theory

The central mathematical object within PFT is the free power functional $\mathcal{R}_t[\rho,\mathbf{J}]$, which depends on time t and is a functional of the density and current [6]. One can split off the external contributions,

$$\mathcal{R}_t[\rho,\mathbf{J}]=W_t[\rho,\mathbf{J}]-\int d\mathbf{r}\,(\mathbf{X}(\mathbf{r},t)-\nabla V_{\mathrm{ext}}(\mathbf{r},t))\cdot\mathbf{J}(\mathbf{r},t) +\int d\mathbf{r}\,\dot{V}_{\mathrm{ext}}(\mathbf{r},t)\,\rho(\mathbf{r},t), \quad (23)$$

where $\mathbf{X}(\mathbf{r},t)$ is a non-conservative external force and the overdot indicates a time derivative of the external potential, which can be time-dependent. The intrinsic part $W_t[\rho,\mathbf{J}]$ of the power functional can be split into two contributions:

$$W_t[\rho,\mathbf{J}]=W_t^{\mathrm{id}}[\rho,\mathbf{J}]+W_t^{\mathrm{exc}}[\rho,\mathbf{J}], \quad (24)$$

where the non-interacting, ideal intrinsic power is given by the sum of dissipative and adiabatic contributions:

$$W_t^{\mathrm{id}}[\rho,\mathbf{J}]=\int d\mathbf{r}\,\frac{\gamma\,\mathbf{J}^2(\mathbf{r},t)}{2\rho(\mathbf{r},t)}+\int d\mathbf{r}\,\mathbf{J}(\mathbf{r},t)\cdot\nabla\frac{\delta F^{\mathrm{id}}[\rho\,]}{\delta\rho(\mathbf{r},t)}, \quad (25)$$

where γ is the friction coefficient (related to the bare diffusion coefficient by $\gamma=k_{\mathrm{B}}T/D_0$), and the ideal gas free-energy functional is given by Equation (9). The excess part of the intrinsic power depends solely upon the interparticle interactions and thus specifies the system under investigation.

The variational principle of PFT implies the minimisation

$$\frac{\delta\mathcal{R}_t[\rho,\mathbf{J}]}{\delta\mathbf{J}(\mathbf{r},t)}=0, \quad (26)$$

where the functional derivative is taken at fixed time, and $\rho(\mathbf{r},t)$ and $\mathbf{J}(\mathbf{r},t)$ are treated as independent fields. In equilibrium, Equation (26) reduces to Equation (8), thus recovering DFT as a special case. Application of Equations (26)–(23) yields a force balance equation as follows:

$$\frac{\gamma\,\mathbf{J}(\mathbf{r},t)}{\rho(\mathbf{r},t)}=-k_{\mathrm{B}}T\nabla\ln\left(\Lambda^3\rho(\mathbf{r},t)\right)+\mathbf{X}(\mathbf{r},t)-\nabla V_{\mathrm{ext}}(\mathbf{r},t) -\frac{\delta W_t^{\mathrm{exc}}[\rho,\mathbf{J}]}{\delta\mathbf{J}(\mathbf{r},t)}. \quad (27)$$

When supplemented by the continuity equation,

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r},t), \tag{28}$$

Equation (27) provides a formally exact equation of motion for the one-body density. However, the excess intrinsic power functional, containing the non-trivial physics, remains to be determined. Expressing this quantity in terms of statistical mechanical correlation functions is the objective of the following section.

4.2. *Functional line integration in PFT*

Many-body Brownian dynamics can be described using the Smoluchowski equation of motion for the N-body configurational probability distribution [15]. Integrating the Smoluchowski equation over all but one of the particle coordinates yields an exact equation for the current [16]:

$$\frac{\gamma \mathbf{J}(\mathbf{r},t)}{\rho(\mathbf{r},t)} = -k_B T \nabla \ln\left(\Lambda^3 \rho(\mathbf{r},t)\right) + \mathbf{X}(\mathbf{r},t) - \nabla V_{\text{ext}}(\mathbf{r},t) - \int d\mathbf{r}' \, \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}',t)}{\rho(\mathbf{r},t)} \nabla \phi(\mathbf{r},\mathbf{r}'), \tag{29}$$

where $\rho^{(2)}(\mathbf{r},\mathbf{r}',t)$ is the non-equilibrium equal-time density correlation function. Comparison of Equation (27) with Equation (29) enables the identification

$$\frac{\delta W_t^{\text{exc}}[\rho,\mathbf{J}]}{\delta \mathbf{J}(\mathbf{r},t)} = \int d\mathbf{r}' \, \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}',t)}{\rho(\mathbf{r},t)} \nabla \phi(\mathbf{r},\mathbf{r}'), \tag{30}$$

which makes explicit the fact that the functional derivative of the excess intrinsic power with respect to the current generates (up to a minus sign) the interparticle interaction forces acting at position $\mathbf{r}$. The right-hand side of Equation (30) is easily generalised to account for triplet and higher body potential interactions [16], but for clarity of presentation, we restrict ourselves to systems with pairwise additive interaction potentials.

Taking Equation (30) as a starting point, we perform a functional line integral to reconstruct the excess intrinsic free power functional. We choose the reference system to be an equilibrium state, $\mathbf{J}_{\text{r}}(\mathbf{r},t) = 0$, and integrate along the parameterised path $\mathbf{J}_\alpha(\mathbf{r},t) = \alpha \mathbf{J}(\mathbf{r},t)$, from $\alpha = 0$ to $\alpha = 1$, while holding the density fixed. This yields

$$W_t^{\text{exc}}[\rho,\mathbf{J}] = \int_0^1 d\alpha \int d\mathbf{r} \, \mathbf{J}(\mathbf{r},t) \cdot \frac{\delta W_t[\rho,\mathbf{J}_\alpha]}{\delta \mathbf{J}_\alpha(\mathbf{r},t)}, \tag{31}$$

where we have used the fact that $W_t^{\text{exc}}[\rho,\mathbf{0}] = 0$ (i.e. for an equilibrium system). The integration in Equation (31) is only over spatial coordinates, because the derivative is taken at fixed time. Substitution of Equation (30) into Equation (31) leads to

$$W_t^{\text{exc}}[\rho,\mathbf{J}] = \int_0^1 d\alpha \int d\mathbf{r} \int d\mathbf{r}' \, \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}',t\,;[\rho,\mathbf{J}_\alpha])}{\rho(\mathbf{r},t)} \times \mathbf{J}(\mathbf{r},t) \cdot \nabla \phi(\mathbf{r},\mathbf{r}'), \tag{32}$$

where we have indicated the functional dependence in the notation explicitly. Equation (32) constitutes an exact relation of the excess intrinsic power functional to a well-defined equal-time pair correlator.

The integral expression (32) has the appealing property that the well-established DDFT is recovered by neglecting the dependence of the integrand on the charging parameter

$$\rho^{(2)}(\mathbf{r},\mathbf{r}',t\,;[\rho,\mathbf{J}_\alpha]) \approx \rho^{(2)}(\mathbf{r},\mathbf{r}',t\,;[\rho,\mathbf{0}\,]). \tag{33}$$

The right-hand side of Equation (33) defines the adiabatic two-body density, $\rho^{(2)}_{\text{ad}}(\mathbf{r},\mathbf{r}',t\,,[\rho\,]) \equiv \rho^{(2)}(\mathbf{r},\mathbf{r}',t\,;[\rho,\mathbf{0}\,])$, namely the two-body density of an *equilibrium* system with one-body density profile $\rho(\mathbf{r},t)$. Substituting Equation (33) into the force integral (30) enables us to use the following equilibrium sum rule [1]:

$$\int d\mathbf{r}' \, \frac{\rho^{(2)}_{\text{ad}}(\mathbf{r},\mathbf{r}',t;\,[\rho\,])}{\rho(\mathbf{r},t)} \nabla \phi(\mathbf{r},\mathbf{r}') = \nabla \frac{\delta F^{\text{exc}}[\rho\,]}{\delta \rho(\mathbf{r},t)}, \tag{34}$$

which relates the interaction forces to the excess Helmholtz free energy. We thus obtain the DDFT approximation to the excess intrinsic power functional

$$W_t^{\text{exc}}[\rho,\mathbf{J}] \;\approx \int d\mathbf{r} \, \mathbf{J}(\mathbf{r},t) \cdot \nabla \frac{\delta F^{\text{exc}}[\rho\,]}{\delta \rho(\mathbf{r},t)}. \tag{35}$$

Equations (27), (28) and (35) recover the familiar DDFT equation for the one-body density [16,17].

4.3. *Exact excess dissipation functional*

We now proceed to further develop the exact expression (32). We will see that this leads to a splitting of the excess intrinsic power into the sum of adiabatic and superadiabatic contributions. Defining the interaction force,

$$\mathbf{f}(\mathbf{r},t\,;[\rho,\mathbf{J}]) \equiv -\frac{\delta W_t^{\text{exc}}[\rho,\mathbf{J}]}{\delta \mathbf{J}(\mathbf{r},t)}, \tag{36}$$

enables Equation (31) to be rewritten as

$$W_t^{\text{exc}}[\rho,\mathbf{J}] = -\int_0^1 d\alpha \int d\mathbf{r} \, \mathbf{J}(\mathbf{r},t) \cdot \mathbf{f}(\mathbf{r},t\,;[\rho,\mathbf{J}_\alpha]). \tag{37}$$

The parameterised force, $\mathbf{f}(\mathbf{r},\,t\,;\,[\rho,\,\mathbf{J}_\alpha])$, that appears in the integrand of Equation (37) can be found by integration of its derivative (starting from an equilibrium reference

state). At this point, it is important to clarify the nature of the functional derivative. The expression (31) involves a space integral, but no time integral, in recognition of the fact that Equation (26), and thus Equation (30), is a functional derivative taken at fixed time. However, when using functional line integration to formally re-express $\mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{J}_\alpha])$, we are no longer constrained by the fixed-time differentiation of the power functional variational principle. The most general choice is to consider functional line integration of the full functional derivative. This yields

$$\mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{J}_\alpha]) = \mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{0}\,]) + \int_0^\alpha d\alpha' \int d\mathbf{r}' \int_{t_0}^t dt'\; J(\mathbf{r}', t') \cdot \frac{\delta \mathbf{f}(\mathbf{r}, t[\rho, \mathbf{J}_\alpha])}{\delta \mathbf{J}_\alpha(\mathbf{r}', t')}, \tag{38}$$

where t_0 is an initial time.

Substitution of Equation (38) into Equation (37) then enables the exact expression (32) for the excess intrinsic power functional to be re-expressed as a sum of two terms:

$$W_t^{\mathrm{exc}}[\rho, \mathbf{J}] = -\int d\mathbf{r}\; \mathbf{J}(\mathbf{r}, t) \cdot \mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{0}\,]). - \int_0^1 d\alpha(1-\alpha) \int d\mathbf{r} \int d\mathbf{r}' \int_{t_0}^t dt'\; \mathbf{J}(\mathbf{r}, t)\mathbf{J}(\mathbf{r}', t') : \times \frac{\delta \mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{J}_\alpha])}{\delta \mathbf{J}_\alpha(\mathbf{r}', t')}, \tag{39}$$

where the colon represents a full contraction between the current–current dyadic and the second-rank tensor functional derivative. The first term in Equation (39) involves the interaction force arising from an inhomogeneous density distribution in equilibrium (vanishing current). Using Equations (30), (34) and (36)), we obtain the exact expression

$$W_t^{\mathrm{exc}}[\rho, \mathbf{J}] = \int d\mathbf{r}\; \mathbf{J}(\mathbf{r}, t) \cdot \nabla \frac{\delta F^{\mathrm{exc}}[\rho\,]}{\delta \rho(\mathbf{r}, t)} - \int_0^1 d\alpha(1-\alpha) \int d\mathbf{r} \int d\mathbf{r}' \int_{t_0}^t dt'\; \mathbf{J}(\mathbf{r}, t)\mathbf{J}(\mathbf{r}', t') : \times \frac{\delta \mathbf{f}(\mathbf{r}, t\,; [\rho, \mathbf{J}_\alpha])}{\delta \mathbf{J}_\alpha(\mathbf{r}', t')}, \tag{40}$$

where the first term now explicitly accounts for the adiabatic intrinsic power. By employing the continuity equation and the functional chain rule, this adiabatic contribution can be identified as the time derivative of the excess free-energy functional, $\dot{F}^{\mathrm{exc}}[\rho\,]$. The second, 'superadiabatic' term describes the excess dissipation due to interparticle interactions. In deriving Equation (40), we have thus found a natural splitting of the excess intrinsic power into adiabatic and superadiabatic contributions:

$$W_t^{\mathrm{exc}}[\rho, \mathbf{J}] = \dot{F}^{\mathrm{exc}}[\rho\,] + P_t^{\mathrm{exc}}[\rho, \mathbf{J}], \tag{41}$$

where the excess dissipation functional, $P_t^{\mathrm{exc}}[\rho, \mathbf{J}]$, corresponds to the second term in Equation (40). The decomposition (41) is identical to the physically motivated splitting introduced in [6].

Differentiation of Equation (36) with respect to the current, at fixed time and using Equation (30) enables the functional derivative of the force appearing in Equation (40) to be expressed in terms of the two-body density correlator:

$$\frac{\delta \mathbf{f}(\mathbf{r}, t; [\rho, \mathbf{J}])}{\delta \mathbf{J}(\mathbf{r}', t')} = \int d\mathbf{r}''\; \frac{\delta \rho^{(2)}(\mathbf{r}, \mathbf{r}'', t\,; [\rho, \mathbf{J}])}{\delta \mathbf{J}(\mathbf{r}', t')}\; \frac{\nabla \phi(\mathbf{r}, \mathbf{r}'')}{\rho(\mathbf{r}, t)}, \tag{42}$$

where the integrand is a dyadic product of two vector functions. Substitution of Equation (42) into Equation (40) yields our final form for the exact excess dissipation functional,

$$P_t^{\mathrm{exc}}[\rho, \mathbf{J}] = \int d\mathbf{r} \int d\mathbf{r}' \int_{t_0}^t dt'\; \mathbf{J}(\mathbf{r}, t) \cdot \times \mathbf{K}(\mathbf{r}, \mathbf{r}', t, t'\,; [\rho, \mathbf{J}]) \cdot \mathbf{J}(\mathbf{r}', t'), \tag{43}$$

where the dyadic matrix Kernel is given exactly by

$$\mathbf{K}(\mathbf{r}, \mathbf{r}', t, t'\,; [\rho, \mathbf{J}]) = \times \int_0^1 d\alpha(1-\alpha) \int d\mathbf{r}''\; \frac{\delta \rho^{(2)}(\mathbf{r}, \mathbf{r}'', t\,; [\rho, \mathbf{J}_\alpha])}{\delta \mathbf{J}_\alpha(\mathbf{r}', t')}\; \frac{\nabla \phi(\mathbf{r}, \mathbf{r}'')}{\rho(\mathbf{r}, t)}. \tag{44}$$

Equations (43) and (44) constitute the main result of the present paper. The excess dissipation functional accounts for the fact that the pair correlations are not equilibrated during the time evolution of the system, and hence corrects the adiabatic approximation. The kernel (44) depends explicitly on the interaction forces and thus, when substituted into Equation (43), corrects the ideal gas dissipation given by the first term in Equation (25). It is intuitive that scattering events arising from the interaction forces will lead to a coupling between different components of the current vector, and this is reflected in the tensorial character of the kernel. For systems under external driving, the ability of the excess dissipation functional to capture non-affine, interaction-induced flows will, in general, be essential to obtain physically realistic predictions (see e.g. [18,19], which highlight some situations where DDFT fails).

Substitution of the split excess intrinsic power (41) into the force balance (27) shows that the interaction-induced dissipative force ('superadiabatic' force) is given by the

derivative

$$\mathbf{F}^{\rm sad}(\mathbf{r},t) = -\frac{\delta P_t^{\rm exc}[\rho,\mathbf{J}]}{\delta \mathbf{J}(\mathbf{r},t)}, \tag{45}$$

with the excess dissipation given by Equation (43). The superadiabatic force has been studied in detail for a simple one-dimensional model, where a non-trivial dependence on particle density was revealed [20].

4.4. *Perturbation approximation*

By neglecting the α-dependence of the integrand (44) and choosing a zero reference current, we obtain the following approximation to the kernel:

$$\mathbf{K}^0(\mathbf{r},\mathbf{r}',t,t';[\rho]) = \int d\mathbf{r}'' \left.\frac{\delta\rho^{(2)}(\mathbf{r},\mathbf{r}'',t;[\rho,\mathbf{J}])}{\delta\mathbf{J}(\mathbf{r}',t')}\right|_{\mathbf{J}=0} \frac{\nabla\phi(\mathbf{r},\mathbf{r}'')}{2\rho(\mathbf{r},t)}, \tag{46}$$

which is a functional of the instantaneous density, but independent of the current. We have thus constructed a leading-order (in current) perturbation theory about the adiabatic state. Equation (46) requires as input the flow-distorted pair correlations close to equilibrium.

It is interesting to note the similarity of the perturbative excess dissipation functional, obtained by substituting Equation (46) into Equation (43), with the exact non-interacting form (the first term in Equation (25)). This suggests to revert to the *total* dissipation as the sum of ideal and excess contributions $P[\rho,\mathbf{J}] = P_t^{\rm id}[\rho,\mathbf{J}] + P_t^{\rm exc}[\rho,\mathbf{J}]$, such that the perturbation approximation to this quantity takes the following form:

$$P_t^0[\rho,\mathbf{J}] = \int d\mathbf{r}\int d\mathbf{r}'\int_{t_0}^{t} dt' \times \frac{\mathbf{J}}{(\mathbf{r},t)\mathbf{J}(\mathbf{r}',t')} 2\rho(\mathbf{r},t) : \boldsymbol{\gamma}^{\mathbf{0}}(\mathbf{r},\mathbf{r}',\mathbf{t},\mathbf{t}';[\rho]), \tag{47}$$

where the effective friction tensor depends solely on the density and is given by

$$\boldsymbol{\gamma}^{\mathbf{0}}(\mathbf{r},\mathbf{r}',\mathbf{t},\mathbf{t}';[\rho]) = \gamma\,\delta(\mathbf{r}-\mathbf{r}')\delta(\mathbf{t}-\mathbf{t}')\mathbf{1} + \int d\mathbf{r}'' \left.\frac{\delta\rho^{(2)}(\mathbf{r},\mathbf{r}'',t;[\rho,\mathbf{J}])}{\delta\mathbf{J}(\mathbf{r}',t')}\right|_{\mathbf{J}=0} \nabla\phi(\mathbf{r},\mathbf{r}''). \tag{48}$$

The first term in Equation (48) generates the exact non-interacting dissipation, while the second term incorporates the spatial non-locality arising from interparticle interactions.

5. Conclusions

In the framework of PFT, we have used the method of functional line integration to derive a formally exact expression for the excess power dissipation functional, given by Equations (43) and (44). The excess dissipation requires as input information about how the inhomogeneous two-body density is distorted by flow (i.e. a non-vanishing current). It is precisely this feature of the non-equilibrium microstructure which is not resolved in the standard, adiabatic DDFT approximation. By neglecting the 'charging' integral in Equation (44), we have generated a perturbation theory about the adiabatic state, characterised by the kernel (46). Given that the adiabatic approximation often performs quite well, we anticipate that using a perturbative excess dissipation functional will generate the most important corrections to DDFT.

In Section 4.3, we employed functional line integration to decompose the excess intrinsic power into a sum of adiabatic and excess dissipation terms. This is certainly a convenient choice for the application of the theory, because it enables the many excellent approximations for the equilibrium free energy to be exploited, but does not represent a fundamental constraint on the theory. The power functional approach is a general and exact dynamical theory, which does not have to make any reference to the adiabatic state. This independence of any adiabatic assumption is made explicit in Section 4.2, where we formulate an exact expression, Equation (32), for the excess intrinsic power, $W_t[\rho,\mathbf{J}]$. This quantity could be made the focus of direct approximation schemes and is the most fundamental object to be approximated within PFT. It is only when one chooses to formulate the theory about the adiabatic state, thus adopting DDFT as a zeroth-order approximation, that the excess dissipated power, $P_t^{\rm exc}[\rho,\mathbf{J}]$, becomes the main object of attention.

For bulk systems, it is known that the flow-induced distortion of the pair correlations contributes to both the shear and bulk viscosities [21]. For general inhomogeneous situations, the excess power dissipation thus takes account of these interaction-induced contributions, which are absent from the ideal dissipation functional and are consequently absent from DDFT. Our formal results provide a solid basis for the development of practical approximation schemes. The next step in our research programme will be to develop and test explicit approximations to the excess dissipation for simple model systems. Work along these lines is in progress.

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